



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 118 637 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.07.2001 Bulletin 2001/30

(51) Int Cl.7: **C08K 5/41, C08L 23/02**

(21) Application number: **01101587.2**

(22) Date of filing: **14.10.1998**

(84) Designated Contracting States:
BE DE FR GB NL

(30) Priority: **16.10.1997 US 951405**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
98953488.8 / 1 023 379

(71) Applicants:
• **ExxonMobil Chemical Patents Inc.**
Baytown, TX 77522 (US)
• **Advanced Elastomer Systems, L.P.**
Akron, Ohio 44311-1059 (US)

(72) Inventors:
• **Pfeiffer, Dennis George**
Annandale, NJ 08801 (US)
• **Ellul, Maria Dolores**
Silver Lake Village, Ohio 44224-2422 (US)
• **Erderly, Thomas Craig**
Baytown, TX 77521 (US)

• **Chludzinski, James Joseph**
White House Station, NJ 08889 (US)
• **Dekmezian, Armenag Hagop**
Kingwood, TX 77345 (US)
• **Hazelton, Donald Ross**
Southport, North Carolina 28461-8035 (US)
• **Montagna, Angelo Anthony**
Houston, TX 77005 (US)
• **Rosenbaum, Barry Martin**
Shaker Heights, Ohio 44118 (US)

(74) Representative:
Veldhulzen, Albert Dirk Willem et al
ExxonMobil Chemical Europe Inc.,
P.O. Box 105
1830 Machelen (BE)

Remarks:

This application was filed on 25 - 01 - 2001 as a
divisional application to the application mentioned
under INID code 62.

(54) **Thermoplastische Elastomierzusammensetzungen mit verbesserten
Verarbeitungseigenschaften**

(57) Thermoplastic elastomers having improved
processability are prepared by incorporating one or
more organic sulfate or sulfonate salts into blends of

thermoplastic polymers and olefinic rubber and melt
processing the mixture. The rubber component of the
mixture is preferably at least partially cured.

EP 1 118 637 A2

Description

[0001] This application is a continuation-in-part of copending U.S. application S.N. 08/906,870, filed August 6, 1997, which is in turn based on provisional application 60/0022432 filed August 6, 1996.

5

BACKGROUND OF THE INVENTION**Field of the Invention**

10 **[0002]** The invention relates to thermoplastic elastomer compositions based on a blend of a thermoplastic material and a cured or non-cured elastomer, and to the processing of such compositions.

Description of Related Art

15 **[0003]** A thermoplastic elastomer is generally defined as a polymer or blend of polymers that can be processed and recycled in the same way as a conventional thermoplastic material, yet has properties and performance similar to that of vulcanized rubber at service temperatures. Blends or alloys of plastic and elastomeric rubber have become increasingly important in the production of high performance thermoplastic elastomers, particularly for the replacement of thermoset rubber in various applications.

20 **[0004]** Polymer blends which have a combination of both thermoplastic and elastic properties are generally obtained by combining a thermoplastic polymer with an elastomeric composition in a way such that the elastomer is intimately and uniformly dispersed as a discrete particulate phase within a continuous phase of the thermoplastic. Early work with vulcanized compositions is found in U.S. Pat. No. 3,037,954 which discloses static vulcanization as well as the technique of dynamic vulcanization wherein a vulcanizable elastomer is dispersed into a resinous thermoplastic polymer and the elastomer is cured while continuously mixing and shearing the polymer blend. The resulting composition is a microgel dispersion of cured elastomer, such as butyl rubber, chlorinated butyl rubber, polybutadiene or polyisoprene in an uncured matrix of thermoplastic polymer such as polypropylene.

25 **[0005]** Depending on the ultimate application, such thermoplastic elastomer (TPE) compositions may comprise one or a mixture of thermoplastic materials such as propylene homopolymers and propylene copolymers and like thermoplastics used in combination with one or a mixture of cured or non-cured elastomers such as ethylene/propylene rubber, EPDM rubber, diolefin rubber, butyl rubber or similar elastomers. TPE compositions may also be prepared where the thermoplastic material used is an engineering resin having good high temperature properties, such as a polyamide or a polyester, used in combination with a cured or non-cured elastomer. Examples of such TPE compositions and methods of processing such compositions, including methods of dynamic vulcanization, may be found in U.S. Patents 4,130,534, 4,130,535, 4,594,390, 5,177,147 and 5,290,886, as well as in WO 92/02582.

30 **[0006]** TPE compositions are normally melt processed using conventional thermoplastic molding equipment such as by injection molding, compression molding, extrusion, blow molding or other thermoforming techniques. In such TPE compositions, the presence of the elastomeric component does not necessarily improve the processability of the composition. In fact, where the elastomeric component is partially or fully cured (cross-linked) in-situ during the mixing of the TPE polymer components (dynamically vulcanized), or where a dynamically vulcanized TPE composition is further processed, there are heavier demands placed upon processing machinery as compared with the processing of a thermoplastic composition which is free of cured elastomer. Increases such as higher motor load, head pressure and/or torque can place undesirable, unacceptable, or unattainable requirements on specific machinery. For instance, a specific extruder having a specific motor power and gearing, will reach a maximum of motor load, or head pressure, under certain melt temperature conditions for a given polymer being processed. If a polymer or polymer blend is introduced to such an extruder which has such a higher requirement for power to process at least one component, such as a polymer having higher molecular weight and/or narrower molecular weight distribution and/or lower shear sensitivity, the extruder will reach a maximum of one or several of these parameters, and be therefore limited in its ability to pump/perform at a similar level to the performance expected with a more easily processable polymer. In the alternative, if melt blending or processing machinery is to be used for certain production/extrusion, and it is not so limited, the prospect of using more power or increasing head pressure for a more difficult to extrude material would be achievable, but the user of the machinery would still nonetheless desire to conserve power.

45 **[0007]** Additionally, TPE compositions may exhibit other imperfections during extrusion, specifically film extrusion, that may be undesirable, such as melt fracture. These imperfections are undesirable from a quality standpoint. For example, melt fracture also known as "shark skin" or "orange peel", can lead to poorer optical properties and/or diminished film physical properties that are generally unacceptable. Adjustments to the extrusion process which are made to avoid the development of melt fracture generally involve a slowing down of the process which leads to a reduced rate of extrudate output.

55

[0008] Various prior art references generally disclose the addition of various additives to olefin polymer compositions to improve the extrusion or other properties of the polymer. For example, GB 1,104,662 teaches addition of the salt of alkyl benzene sulfonic acids to polyolefins that purportedly gives a beneficial effect on melt extrusion behavior of the polyolefin. The purported effect is the reduction of the occurrence of "shark skin" or "orange peel". Both alkali and alkaline earth metal salts of alkyl benzene sulfonic acids are said to be effective.

[0009] GB 1,078,738 discloses that addition of an "external lubricant" to high molecular weight polyolefins can, purportedly, reduce occurrence of melt fracture. Suggested as external lubricants are salts of monovalent to tetravalent metals, and saturated or unsaturated carboxylic acids containing 10 to 50 carbon atoms. Sulfonates corresponding to the fatty acid salts are also said to be suitable.

[0010] JP A 59-176339 discloses that when polyolefins are narrowed in MWD or given higher molecular weight, poor fluidity results which in turn gives rise to melt fracture. The solution suggested is addition of fluorinated compounds including potassium salts of fluoroalkylsulfonic acids. These potassium salts are said to exhibit preferable temperature dependence when compared to other cations such as sodium, calcium, lithium and ammonium. The polyolefin/salt combination is said to be effective at 230° C or higher.

[0011] DE 2,823,507 discloses calendered ethylene polymers and propylene polymers containing alkali or alkaline earth mono sulfonates such as alkyl sulfonates, alenyl sulfonates, alkylaryl sulfonates and succinic acid dialkyl ester sulfonates. Sodium or calcium mono sulfonates are preferred. A suggested benefit is purported to be outstanding separation of the polymer from calendering rolls.

[0012] Canadian Patent 731,225 discloses the use of alkali metal salts of certain monosulfonic acids as additives to crystallizable polypropylene compositions to modify the crystallization properties of the polymer. Although these compositions may also include an elastomeric polymer as an impact modifier, the reference does not indicate that the additives improve polymer processability.

[0013] There is a need therefore for a relatively inexpensive, easily implemented solution to the processing problems outlined above. Such a solution should also include a material that will readily melt or incorporate into the melted TPE and not adversely affect physical properties, not interfere with crosslinking chemistry or structure produced by that chemistry, not be extractable, or negatively impact organoleptics of shaped TPE articles. Specifically, there is a commercial need for a material that may be easily incorporated into TPE compositions, that will reduce or eliminate the increased power requirement (e.g., motor load and or torque) and increased head pressure.

SUMMARY OF THE INVENTION

[0014] This invention provides a thermoplastic elastomer composition comprising a blend of: a) a thermoplastic polymer; b) an olefinic rubber; and c) from 0.005 to 5 wt%, based on the polymeric content of said blend, of at least one sulfate or sulfonate salt having the formula $(R-SO_x)_M$ where X is 3 or 4, R is an organic aliphatic radical containing from 6 to 30 carbon atoms and M is a cation selected from the group consisting of alkali metals, alkaline earth metals and ammonium

[0015] The invention also provides a process for forming a composition or an extruded article comprising melt blending a thermoplastic elastomer composition comprising a blend of: a) a thermoplastic polymer; b) an olefinic rubber; and c) from 0.005 to 5 wt%, based on the polymeric content of said blend, of at least one sulfate or sulfonate salt having the formula $(R-SO_x)_M$ where X is 3 or 4, R is an organic aliphatic radical containing from 6 to 30 carbon atoms and M is a cation selected from the group consisting of alkali metals, alkaline earth metals and ammonium.

[0016] The invention is based on the discovery that inclusion of the above-described sulfate or sulfonate salts in TPE molding compositions results in a marked reduction of the energy requirements for melt processing and extrusion of conventional TPE compositions. In addition, injection mold spiral flow lengths are increased and fill times are significantly lowered which leads to reduced cycle times in injection molding processes.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Following is a description of the various ingredients which may be used to formulate the TPE compositions of this invention.

Thermoplastic Polymer

[0018] Thermoplastic polymers suitable for use in the present invention include amorphous, partially crystalline or essentially totally crystalline polymers selected from the group consisting of polyolefins, polyamides, polyimides, polyesters, polycarbonates, polysulfones, polylactones, polyacetals, acrylonitrile/butadiene/ styrene copolymer resins, polyphenylene oxides, ethylene-carbon monoxide copolymers, polyphenylene sulfides, polystyrene, styrene/ acrylonitrile copolymer resins, styrene/maleic anhydride copolymer resins, aromatic polyketones and mixtures thereof

[0019] Polyolefins suitable for use in the compositions of the invention include thermoplastic, at least partially crystalline polyolefin homopolymers and copolymers, including polymers prepared using Ziegler/Natta type catalysts or metallocene catalysts. They are desirably prepared from monoolefin monomers having 2 to 6 carbon atoms, such as ethylene, propylene, 1-butene, isobutylene, 1-pentene, copolymers containing these monomers, and the like, with propylene being the preferred monomer. As used in the specification and claims, the term polypropylene includes homopolymers of propylene as well as reactor copolymers of propylene which can contain 1 to 20 wt% of ethylene or an alpha-olefin comonomer of 4 to 16 carbon atoms or mixtures thereof. The polypropylene can be highly crystalline isotactic or syndiotactic polypropylene, usually having a narrow range of glass transition temperature (T_g). Commercially available polyolefins may be used in the practice of the invention.

[0020] Suitable thermoplastic polyamides (nylons) comprise crystalline or resinous, high molecular weight solid polymers including copolymers and terpolymers having recurring amide units within the polymer chain. Polyamides may be prepared by polymerization of one or more epsilon lactams such as caprolactam, pyrrolidione, lauryllactam and aminoundecanoic lactam, or amino acid, or by condensation of dibasic acids and diamines. Both fiber-forming and molding grade nylons are suitable. Examples of such polyamides are polycaprolactam (nylon 6), polylauryllactam (nylon 12), polyhexamethyl-eneadipamide (nylon-6,6), polyhexamethyleneazelaamide (nylon -6,9), polyhexamethylenesebacamide (nylon 6,10), polyhexa-methyleneisophthalamide (nylon-6,1P) and the condensation product of 11-amino-undecanoic acid (nylon 11). Commercially available thermoplastic polyamides may be advantageously used in the practice of this invention, with linear crystalline polyamides having a softening point or melting point between 160°C-230°C being preferred.

[0021] Suitable thermoplastic polyesters which may be employed include the polymer reaction products of one or a mixture of aliphatic or aromatic polycarboxylic acids esters of anhydrides and one or a mixture of diols. Examples of satisfactory polyesters include poly (trans-1,4-cyclohexylene C_{2-6} alkane dicarboxylates such as poly(trans-1,4-cyclohexylene succinate) and poly (trans-1,4-cyclohexylene adipate); poly (cis or trans- 1,4-cyclohexanedimethylene) alkanedicarboxylates such as poly(cis 1,4-cyclohexane-di-methylene) oxlate and poly-(cis 1,4-cyclohexane-di- methylene) succinate, poly (C_{2-4} alkylene terephthalates) such as polyethyl-eneterephthalate and polytetramethylene-terephthalate, poly (C_{2-4} alkylene isophthalates such as polyethyleneisophthalate and polytetramethylene-isophthalate and like materials. Preferred polyester are derived from aromatic dicarboxylic acids such as naphthalenic or phthalic acids and C_2 to C_4 diols, such as polyethylene terephthalate and polybutylene terephthalate. Preferred polyesters will have a melting point in the range of 160°C to 260°C.

[0022] Poly(phenylene ether) (PPE) thermoplastic engineering resins which may be used in accordance with this invention are well known, commercially available materials produced by the oxidative coupling polymerization of alkyl substituted phenols. They are generally linear polymers having a glass transition temperature in the range of 190°C to 235°C. Examples of preferred PPE polymers include poly(2,6-dialkyl-1,4 phenylene ethers) such as poly(2,6 dimethyl-1,4-phenylenether), poly 2-methyl-6-ethyl-1, 4 phenylene ether), poly-(2,6-dipropyl-1,4-phenylene ether) and poly (2-ethyl-6-propyl-1,4-phenylene ether). These polymers, their method of preparation and blends with polystyrene are further described in U.S. Patent 3,383,435, the complete disclosure of which is incorporated herein by reference.

[0023] Other thermoplastic resins which may be used include the polycarbonate analogs of the polyesters described above such as segmented poly(ether co-phthalates); polycaprolactone polymers; styrene resins such as copolymers of styrene with less than 50 mole% of acrylonitrile (SAN) and resinous copolymers of styrene, acrylonitrile and butadiene (ABS); sulfone polymers such as polyphenyl sulfone, and like engineering resins as are known in the art.

Olefinic Rubber

[0024] Suitable rubbery materials which may be used include monoolefin copolymeric rubbers, isobutylene copolymers and diolefin rubbers, as well as mixtures thereof.

[0025] Suitable monoolefin copolymer rubbers comprise non-polar, essentially non-crystalline, rubbery copolymers of two or more alpha-monoolefins, preferably copolymerized with at least one polyene, usually a diene. Saturated monoolefin copolymer rubber, for example ethylene-propylene copolymer rubber (EPM) can be used. However, unsaturated monoolefin rubber such as EPDM rubber is more suitable. EPDM is a terpolymer of ethylene, propylene and a non-conjugated diene. Satisfactory non-conjugated dienes include 5-ethylidene-2-norbornene (ENB); vinylnorbornene (VNB) 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene, 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and the like.

[0026] Butyl rubbers are also useful in the compositions of the invention. As used in the specification and claims, the term "butyl rubber" includes copolymers of an isoolefin and a conjugated monoolefin, terpolymers of an isoolefin, a conjugated monoolefin and divinyl aromatic monomers, and the halogenated derivatives of such copolymers and terpolymers. The useful butyl rubber copolymers comprise a major portion of isoolefin and a minor amount, usually less than 30 wt%, of a conjugated multiolefin, and are preferably halogenated, e.g., brominated, to facilitate curing. The preferred copolymers comprise 85-99.5 wt% of a C_{4-7} isoolefin such as isobutylene and 15-0.5 wt% of a multiolefin of

4-14 carbon atoms, such as isoprene, butadiene, dimethyl butadiene and piperylene. Commercial butyl rubber, useful in the invention, is a copolymer of isobutylene and minor amounts of isoprene. Other butyl co- and terpolymer rubbers are illustrated by the description in U.S. Patent No. 4,916,180, which is fully incorporated herein by this reference.

5 [0027] Another suitable copolymer within the scope of the olefinic rubber of the present invention is a copolymer of a C₄₋₇ isomonoolefin and a para-alkylstyrene, and preferably a halogenated derivative thereof. The amount of halogen in the copolymer, predominantly present as benzylic halogen, is from 0.1 to 10 wt%. A preferred example is the brominated copolymer of isobutylene and para-methylstyrene. These copolymers are more fully described in U.S. Patent No. 5,162,445, which is fully incorporated herein by reference.

10 [0028] Another olefinic rubber class which may be used are diolefins such as polybutadiene as well as elastomeric random copolymers of butadiene with less than 50 wt% of styrene or acrylonitrile. Other suitable diolefin materials include natural rubber or synthetic polyisoprene. Mixtures comprising two or more of the olefinic rubbers may also be used.

15 [0029] Depending upon the desired applications, the amount of olefinic rubber present in the composition may range from 10 to 90 wt% of the total polymer content of the composition. In most applications and particularly where the rubber component is dynamically vulcanized, the rubber component will constitute less than 70 wt%, more preferably less than 50 wt%, and most preferably 10-40 wt% of the total polymer content of the composition.

Surfactants

20 [0030] The surfactants useful in the present invention include one or a mixture of sulfate and sulfonate salts having the generic formula (RSO_x)_M wherein X is 3 or 4, R is an organic radical containing from 6 to 30 carbon atoms and M is a cation selected from the group consisting of alkali metals, alkaline earth metals and ammonium. Materials of this type are well known in the detergent art and are commercially available.

25 [0031] Preferred surfactants are those where R is a branched or straight chain aliphatic group including alkyl, mono or di unsaturated alkenyl, alkoxy, hydroxy substituted alkyl or alkoxy alkyl. M is preferably selected from lithium, sodium, potassium, calcium or magnesium, with sodium most preferred. M may also be an ammonium cation or a quaternary ammonium cation. Suitable surfactants include sodium lauryl sulfate or sulfonate, sodium alpha olefin sulfonate, ammonium lauryl sulfate, ammonium lauryl sulfonate, sodium myristyl sulfate or sulfonate, sodium octyl sulfate, and like materials. Preferred surfactants are those where R contains 8 to 20 carbon atoms, more preferably 12 to 18 carbon atoms and where R is free of halogen, e.g., fluorine substituent groups and does not contain aromatic groups.

30 [0032] The selection of particular surfactant is dictated by the fact that the melting point of the surfactant should be lower than the temperature at which the polymer composition is processed, and preferably be lower than the softening or melting point of the thermoplastic polymer component (and the rubber component) present in the blend, preferably at least 10°C lower. Since the surfactant appears to function as an external lubricant during processing, it is important that it be in the melt state along with the molten polymers being processed. Thus preferred surfactants are those with a melting point below 240°C, more preferably below 230°C and most preferably below 210°C, e.g., sodium lauryl sulfate or sulfonate or sodium alpha olefin sulfonates. On the other hand where the thermoplastic polymer being processed is of relatively high melting point, e.g., polyamides, then higher melting point surfactants may be used, e.g., the alkaline earth metal sulfate or sulfonate salts.

40 [0033] Another factor dictating the choice of surfactant is that it should be insoluble or only sparingly soluble in liquid or semi-liquid additive materials included in the composition, such as processing oils. Severe dilution of the surfactant by such additives will result in a diminution or loss of the enhanced melt processing characteristics of the surfactant.

[0034] The surfactant may be incorporated into the composition at a level of from 0.005 to 5 wt%, more preferably from 0.01 to 0.5 wt% and most preferably from 0.03 to 0.35 wt%, based on the polymeric content of the blend.

Additives

50 [0035] The compositions of the invention may include plasticizers, curatives and may also include reinforcing and non-reinforcing fillers, antioxidants, stabilizers, rubber processing oil, plasticizers, extender oils, lubricants, antiblocking agents, anti-static agents, waxes, foaming agents, pigments, flame retardants and other processing aids known in the rubber compounding art. Such additives can comprise up to 50 wt% of the total composition. Fillers and extenders which can be utilized include conventional inorganics such as calcium carbonate, clays, silica, talc, titanium dioxide, carbon black and the like. The rubber processing oils generally are paraffinic, naphthenic or aromatic oils derived from petroleum fractions, but are preferably paraffinic. The type will be that ordinarily used in conjunction with the specific rubber or rubbers present in the composition, and the quantity based on the total rubber content may range from zero up to 1-200 parts by weight per hundred rubber (phr). Plasticizers such as trimellitate esters may also be present in the composition.

Processing

5 **[0036]** The olefin rubber component of the thermoplastic elastomer is generally present as small, i.e., micro-size, particles within a continuous plastic matrix, although a co-continuous morphology or a phase inversion is also possible depending on the amount of rubber relative to plastic, and the cure system or degree of cure of the rubber. The rubber is desirably at least partially crosslinked, and preferably is completely or fully cross-linked. The partial or complete crosslinking can be achieved by adding an appropriate rubber curative to the blend of thermoplastic polymer and rubber and vulcanizing the rubber to the desired degree under conventional vulcanizing conditions. However, it is preferred that the rubber be crosslinked by the process of dynamic vulcanization. As used in the specification and claims, the

10 term "dynamic vulcanization" means a vulcanization or curing process for a rubber contained in a thermoplastic elastomer composition, wherein the rubber is vulcanized under conditions of high shear at a temperature above the melting point of the component thermoplastic. The rubber is thus simultaneously crosslinked and dispersed as fine particles within the matrix thermoplastic, although as noted above other morphologies may also exist. Dynamic vulcanization is effected by mixing the thermoplastic elastomer components at elevated temperature in conventional mixing equipment such as roll mills, Banbury mixers, Brabender mixers, continuous mixers, mixing extruders and the like. The

15 unique characteristic of dynamically cured compositions is that, notwithstanding the fact that the rubber component is partially or fully cured, the compositions can be processed and reprocessed by conventional plastic processing techniques such as extrusion, injection molding, blow molding and compression molding. Scrap or flashing can be salvaged and reprocessed.

20 **[0037]** Those ordinarily skilled in the art will appreciate the appropriate quantities, types of cure systems and vulcanization conditions required to carry out the vulcanization of the rubber. The rubber can be vulcanized using varying amounts of curative, varying temperatures and varying time of cure in order to obtain the optimum crosslinking desired. Any known cure system for the rubber can be used, so long as it is suitable under the vulcanization conditions with the specific olefinic rubber or combination of rubbers being used and with the thermoplastic component. These curatives

25 include sulfur, sulfur donors, metal oxides, resin systems, peroxide-based systems, hydrosilation curatives, containing platinum or peroxide catalysts, and the like, both with and without accelerators and co-agents. Such cure systems are well known in the art and literature of vulcanization of elastomers.

[0038] The terms "fully vulcanized" and "completely vulcanized" as used in the specification and claims mean that the rubber component to be vulcanized has been cured to a state in which the elastomeric properties of the crosslinked

30 rubber are similar to those of the rubber in its conventional vulcanized state, apart from the thermoplastic elastomer composition. The degree of cure can be described in terms of gel content or, conversely, extractable components. Alternatively the degree of cure may be expressed in terms of crosslink density. All of these descriptions are well known in the art, for example in U.S. Patent Nos. 5,100,947 and 5,157,081, both of which are fully incorporated herein by reference.

35 **[0039]** The processing surfactants may be included in the composition during the manufacture of the TPE composition by processes as described above, or may be later combined with pelletized TPE compositions used by a processor to manufacture shaped articles. For example, TPE extruded pellets may be thoroughly mixed with the surfactant in finely divided powder or liquid form to thoroughly coat each pellet, and the -coated pellets introduced into an extruder along with any other additives used by the processor to produce extruded shaped articles by such process as injection

40 molding, compression molding, blow molding and similar extrusion processes.

[0040] Melt processing temperatures will generally range from above the melting point of the highest melting polymer present in the TPE composition up to 300°C. Preferred processing temperatures will range from 140°C up to 250°C, more preferably from 150°C up to 225°C.

[0041] The following examples are illustrative of the invention.

45 **[0042]** TPE compositions used in the following examples are as follows:

TPE-U A thermoplastic elastomer comprising a mixture of 100 parts by weight of EPDM rubber (VISTALON® 7500 supplied by Exxon Chemical Co.) and 50 parts by weight of isotactic polypropylene.

50 TPE-DO A dynamically vulcanized version of TPE-U cured using a phenolic resin curing system and containing 107 parts by weight of paraffin oil per 100 parts by weight of EPDM.

TPE-DN A dynamically vulcanized thermoplastic elastomer cured using a phenolic resin curing system and based on a mixture of 100 parts by weight of an elastomeric copolymer of butadiene and acrylonitrile, 35 parts by weight of isotactic polypropylene, and 50 parts by weight of a trimellitate ester plasticizer.

55 TPE-DS A dynamically vulcanized blend of 100 parts by weight EPDM rubber, 41 parts by weight of isotactic polypropylene and 130 parts by weight of paraffin oil cured using a phenolic resin curing system

TPE-DSA Same as TPE-DS but containing 220 parts by weight isotactic polypropylene and 100 parts by weight EPDM rubber.

TPE-DSB A dynamically vulcanized blend of 100 parts by weight EPDM rubber, 50 parts by weight isotactic polypro-

EP 1 118 637 A2

pylene, 176 parts by weight processing oil and cured using a hydrosilation cure system.

TPE-DXL A dynamically vulcanized blend of EPDM rubber and polyolefin, containing low amounts of hydrocarbon oil and cured with a peroxide cure system.

TPE-DT A dynamically vulcanized blend of butyl rubber, isotactic polypropylene, oil and curatives.

5

EXAMPLE 1

[0043] This example demonstrates a reduction in torque (as measured by changes in amperage) of compositions of this invention when melt processed. A pelletized form of the TPE compositions listed in Table 1 were each introduced into a Brabender™ Plasti-Corder melt mixer which was heated at 200°C. Typically, 50-60 g. of material is introduced at a rotation speed of 40 RPM. Upon complete melting, the torque remains essentially invariant with time and is used as the base value. Subsequently, measured amounts of sodium alpha-olefin sulfonate surfactant (Bio Terge® AS-90 marketed by Stepan Co., Northfield, Ill.) were added to each sample in the amounts listed in Table 1. After several minutes of mixing, the torque was again measured at 40 RPM and compared with the base value for each sample. As shown in Table 1, torque reductions ranging from 7.9 to 16.0% were achieved.

10

15

TABLE 1

Sample	Surfactant CONC, (ppm)	Torque Reduction (%)
TPE-U	3500	7.9
TPE-U	5000	16.0
TPE-DO	3500	9.3
TPE-DO	5000	12.0
TPE-DN	3500	11.3
TPE-DN	5000	16.0

20

25

EXAMPLE 2

30

[0044] This example illustrates the effect of surfactants of this invention on extrusion properties. TPE-DS thermoplastic elastomer identified above in pellet form was tumbled in a drum with 1.14 g. HT100 mineral oil per pound of TPE-DS. The surfactant in powder form was then added at the levels shown in Table 2 and the material was tumbled another ½ hour to uniformly coat the pellets. Comparative samples of TPE-DS coated with a known processing aid (Dow Corning MB50-001 silicone rubber concentrate) were also prepared. The material identified in Table 2 as "AOK" is also a sodium salt of an alpha-olefin sulfonate available from Witco Chemical Co., Greenwich, CT. Prior to extrusion, the coated materials were run into a Berstorff ZE-43 extruder at 350 rpm and at 234°C to homogenize the dispersion. The torque for each sample processed in the extruder was measured in Amps and results are shown in Table 2.

35

40

TABLE 2

	Torque	% Reduction Torque
Control TPE-DS	33	0.0
0.35% AS-90	31	6.1
0.5% AS-90	29	12.1
0.35% AOK	33	0.0
0.5% AOK	28	15.2
5% AOK	26	21.2
0.5% MB50-001	33	0.0
5% MB50-001	31	6.1

45

50

[0045] Samples as shown in Table 2 were then fed into a Killion 3 horsepower extruder heated to a 3 zone temperature ranging from 190°C to 200°C and extruded into ribbon through a 0.020 inch slit die at a melt temperature of 215°C. Extruder parameters for each sample processed are shown in Table 3.

55

TABLE 3

Extruder Parameters	Head Pressure psi	Amps	Lb/hr*	% Reduction Amps	% Change lb/hr	
Control TPE-DS	450	2.7	5.16	0.0	0.0	
0.35% AS-90	440	2.4	5.24	2.2	1.6	
0.5%AS-90	430	2.4	5.24	4.4	1.6	
0.35% AOK	430	2.4	4.92	4.4	-4.7	Slippage Minor
0.5% AOK	420	2.1	4.88	6.7	-5.4	Slippage Minor
5%AOK**	250	1.5	5.20	44.4**	0.8	
0.5% MB50-001	450	2.4	5.16	0.0	0.0	
5% MB50-001	380	2.1	4.6	15.6	-10.9	Slippage

* Output measured after 3 min run. Between runs the material was extruded for 15 mins before any readings or output measurements were taken. Between materials a purge was made.
 **Duplicated 3 times.

[0046] The parameters as measured in Table 3 demonstrate a general reduction in extruder head pressure and torque as measured by the Amps Output rate as measured in lb/hour was also not compromised and in most cases increased as compared with the control containing no processing aid. In contrast, the comparative samples containing 5% silicone polymer showed significant slippage and therefore a loss of output.

EXAMPLE 3

[0047] The same materials as described in Example 2 were injection molded using a Cincinnati Millacron 250 ton injection molder operating under the following conditions:

Machine Heat Settings	- Rear 182°C, Center 188°C, Front 194°C, Nozzle 200°C.
Melt temperature	- 210°C
Shot Size	- 0.85 inch
Cushion	- 0.19 inch
Screw	- 100 rpm
Ram Velocity	- 3.0 inch/sec.

[0048] Injection molding results using an 1 S0 standard mold to make plaques of 2 mm thickness are shown in Table 4.

TABLE 4

	Fill time (sec)	Pack (sec)	Hold (sec)	Cooling (sec)	Press. 1 st Stage psi	Press Back Psi	Press. Hold Psi	Press. Back Psi
CONTROL TPE-DS	1.42	3.0	2.0	30.0	609	350	200	0
0.35%AS-90	2.167	3.0	2.0	30.0	605	350	200	0
0.5% AS-90	0.63	3.0	2.0	25.0	578	350	200	0

EP 1 118 637 A2

TABLE 4 (continued)

	Fill time (sec)	Pack (sec)	Hold (sec)	Cooling (sec)	Press. 1 st Stage psi	Press Back Psi	Press. Hold Psi	Press. Back Psi	
5	0.35% AOK	0.55	3.0	2.0	25	602	350	200	0
	0.5% AOK	0.6	3.0	2.0	30.0	605	350	200	0
10	5% AOK	0.49	3.0	2.0	25.0	580	350	200	0
	0.5% MB50-001	0.94	3.0	2.0	30.0	589	350	200	0
15	5% MB50-001	--	3.0	2.0	25	602	350	200	0

[0049] As shown in Table 4, the general effect of the use of the surfactants of this invention is to lower the fill time up to a factor of three, which thereby represents a potential of lowering the overall cycle time. It was also observed that at all pressures there was a significant improvement in spiral flow for additives used at the 5% by weight level. Also, mold sticking was observed in all samples containing the silicone polymer, but no mold sticking took place in samples containing the surfactants of this invention.

EXAMPLE 4

[0050] Compositions as identified in Table 5 were coated with the identified additive in the levels indicated and processed through a Berstorff extruder as described in Example 2. Viscosity measurements and torque reductions for each processed TPE sample were compared with TPE controls containing no added processing aid. ACR viscosity is shear viscosity measured using a Monsanto automatic capillary rheometer; extensional viscosity is measured using a Goettfert Rheotens rheometer.

TABLE 5

Extruder Parameters	Torque Amps	% Reduc. Torque	Melt Press.	Ext. Visc. at 190°C kPa s	% Reduc. Ext. Visc.	ACR Visc. at 204°C Poise	% Reduc. ACR Visc.
SAMPLE							
Control TPE-DS	42	0.0	1256	51.4	0.0	183	0.0
+0.5% AOK	42	0.0	1254	47.3	8.0	148	19.1
+1% AOK	38	9.5	1165	50.5	1.8	151	17.5
+2% AOK	38	9.5	1140	45.6	11.3	140	23.5
Control TPE-DT	47	0.0	1733	91.9	0.0	927	0.0
+0.5% AOK	45	4.3	1615	95.2	3.6	829	10.6
+1% AOK	43	8.5	1580	83.5	9.1	876	5.5
+2% AOK	40	4.8	1431	78.2	14.9	746	19.5
Control TPE-DSB	34	0.0	1292	70.3	0.0	173	0.0
+1% AOK	32	5.9	1187	89.5	27.3	111	35.8
Control TPE-DXL	62	0.0	2284	639	0.0	12144	0.0
+1% AOK	54	12.9	1991	248	61.2	1550	87.2

EP 1 118 637 A2

TABLE 5 (continued)

Extruder Parameters	Torque Amps	% Reduc. Torque	Melt Press.	Ext. Visc. at 190°C kPa s	% Reduc. Ext. Visc.	ACR Visc. at 204°C Poise	% Reduc. ACR Visc.
SAMPLE							
Control TPE-DSA	46	0.0	2134	586	0.0	671	0.0
+0.5% AOK	43	6.5	2096	620	5.8	526	21.6
+1% AOK	40	13.0	1906	444	24.2	444	33.8
+2% AOK	33	21.4	1709	402	31.4	372	44.6

[0051] Results in Table 5 show a general reduction in torque for samples containing additive vs control samples free of additive and also a general reduction in extruder melt pressure, indicating improved flow. Reductions in extensional viscosity and ACR viscosities are also demonstrated as compared with the controls.

Claims

1. A thermoplastic elastomer composition comprising a blend of:
 - a) a thermoplastic polymer;
 - b) a crosslinked olefinic rubber; and
 - c) from 0.005 to 5 wt%, based on the polymeric content of said blend, of at least one sulfate or sulfonate salt having the formula $(RSO_x)_M$ wherein X is 3 or 4, R is an organic aliphatic radical containing from 6 to 30 carbon atoms and M is a cation selected from the group consisting of alkali metals, alkaline earth metals and ammonium.
2. The composition of claim 1 wherein said salt has a melting point lower than the softening point of said thermoplastic polymer; wherein said olefinic rubber is present in said composition at a level of 10 to 90 wt% based on the total polymer content of said composition; wherein said thermoplastic polymer is a crystalline polyolefin homopolymer or copolymer, preferably wherein said crystalline polyolefin is polypropylene or a copolymer of propylene with 1-20 wt% of ethylene or an alpha-olefin comonomer of 4-16 carbon atoms or mixtures thereof.
3. The composition of any of the preceding claims wherein said salt is an alkali metal salt or an alkyl or alkenyl sulfonate containing 12 to 18 carbon atoms, preferably wherein said salt is a sodium alpha-olefin sulfonate; and wherein said salt is present in said composition at a level of from 0.01 to 0.5 wt%.
4. The composition of any of the preceding claims wherein said olefinic rubber is selected from the group consisting of ethylene/propylene copolymers, ethylene/propylene/non-conjugated diene terpolymers, isobutylene copolymers, diolefin polymers and copolymers, and mixtures thereof; and wherein the composition further contains a rubber processing oil in said composition at a level of from 1-200 parts by weight phr.
5. The composition of any of the preceding claims wherein said olefinic rubber is crosslinked by dynamic vulcanization.



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 118 637 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
05.12.2001 Bulletin 2001/49

(51) Int Cl.7: **C08K 5/41, C08K 5/42,
C08L 23/02**

(43) Date of publication A2:
25.07.2001 Bulletin 2001/30

(21) Application number: **01101587.2**

(22) Date of filing: **14.10.1998**

(84) Designated Contracting States:
BE DE FR GB NL

(30) Priority: **16.10.1997 US 951405**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
98953488.8 / 1 023 379

(71) Applicants:
• **ExxonMobil Chemical Patents Inc.
Baytown, TX 77522 (US)**
• **Advanced Elastomer Systems, L.P.
Akron, Ohio 44311-1059 (US)**

(72) Inventors:
• **Pfeiffer, Dennis George
Annandale, NJ 08801 (US)**
• **Ellul, Maria Dolores
Silver Lake Village, Ohio 44224-2422 (US)**

• **Erderly, Thomas Craig
Baytown, TX 77521 (US)**
• **Chludzinski, James Joseph
White House Station, NJ 08889 (US)**
• **Dekmezian, Armenag Hagop
Kingwood, TX 77345 (US)**
• **Hazelton, Donald Ross
Southport, North Carolina 28461-8035 (US)**
• **Montagna, Angelo Anthony
Houston, TX 77005 (US)**
• **Rosenbaum, Barry Martin
Shaker Heights, Ohio 44118 (US)**

(74) Representative:
**Veldhuizen, Albert Dirk Willem et al
ExxonMobil Chemical Europe Inc.,
P.O. Box 105
1830 Machelen (BE)**

(54) **Thermoplastische Elastomerzusammensetzungen mit verbesserten
Verarbeitungseigenschaften**

(57) Thermoplastic elastomers having improved
processability are prepared by incorporating one or
more organic sulfate or sulfonate salts into blends of

thermoplastic polymers and olefinic rubber and melt
processing the mixture. The rubber component of the
mixture is preferably at least partially cured.

EP 1 118 637 A3



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 1587

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 266 596 A (GEN. ELECTRIC) 11 May 1988 (1988-05-11) * page 6, line 40 - line 43; claims 1,5,6,8,14,18; examples 4,6 *	1,3	C08K5/41 C08K5/42 C08L23/02
X	* page 7, line 33 - line 35 *	1	
A	GB 1 155 353 A (SUMITOMO) 18 June 1969 (1969-06-18) * page 1, column 2, line 70 - line 81 * * claims 1-5,8; examples 4-6 *	1,4	
A	EP 0 336 573 A (ICI) 11 October 1989 (1989-10-11) * claims 1,5,9 *	1,4	
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 254 (C-308), 11 October 1985 (1985-10-11) & JP 60 106846 A (MITSUI SEKIYU KAGAKU KOGYO KK), 12 June 1985 (1985-06-12) * abstract * -& DATABASE WPI Derwent Publications Ltd., London, GB; AN 86-071418 XPO02095377 * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 October 2001	Examiner Engel, S
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03 02 (F04U01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 01 10 1587

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11-10-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 266596	A	11-05-1988	US 4873277 A	10-10-1989
			DE 3779721 D1	16-07-1992
			DE 3779721 T2	04-02-1993
			EP 0266596 A2	11-05-1988
			JP 63152661 A	25-06-1988
GB 1155353	A	18-06-1969	DE 1694911 A1	06-05-1971
			FR 1509592 A	28-03-1968
			NL 6701323 A	31-07-1967
EP 336573	A	11-10-1989	AT 124710 T	15-07-1995
			AU 3167489 A	05-10-1989
			CA 1339941 A1	07-07-1998
			DE 68923308 D1	10-08-1995
			DE 68923308 T2	26-10-1995
			EP 0336573 A1	11-10-1989
			ES 2074464 T3	16-09-1995
			GR 3017476 T3	31-12-1995
			JP 1289847 A	21-11-1989
			KR 128905 B1	07-04-1998
			NZ 228399 A	26-02-1991
			US 5013778 A	07-05-1991
			US 5112894 A	12-05-1992
JP 60106846	A	12-06-1985	JP 1689886 C	27-08-1992
			JP 3052781 B	13-08-1991

EPO FORM P0458

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82